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Technical Note

1967-38

Growth of Single Ti_2O_3 Crystals from the Melt

T. B. Reed
R. E. Fahey
J. M. Honig

11 August 1967

Prepared under Electronic Systems Division Contract AF 19(628)-5167 by

Lincoln Laboratory
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Lexington, Massachusetts

AD0657978

The work reported in this document was performed at Lincoln Laboratory, a center for research operated by Massachusetts Institute of Technology, with the support of the U.S. Air Force under Contract AF 19(628)-5167.

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MASSACHUSETTS INSTITUTE OF TECHNOLOGY

LINCOLN LABORATORY

GROWTH OF SINGLE Ti_2O_3 CRYSTALS FROM THE MELT

T. B. REED
R. E. FAHEY
J. M. HONIG

Group 83

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ABSTRACT

Procedures are described for growth of large single crystals of TiO_x, $(1.501 \leqslant x \leqslant 1.512)$ that are reasonably free of cationic impurities and of C and N. Data concerning the stoichiometry and the segregation of impurities during crystal growth are presented. The electrical properties of doped and pure single crystal materials are briefly described.

Accepted for the Air Force
Franklin C. Hudson
Chief, Lincoln Laboratory Office

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GROWTH OF SINGLE Ti_2O_3 CRYSTALS FROM THE MELT

I. INTRODUCTION

Titanium sesquioxide is an electronic material which exhibits marked changes in electrical characteristics with temperature. As part of a research program in this Laboratory, it was found necessary to grow large single crystals of Ti_2O_3 for a study of the anisotropy in electrical and optical properties, pure single crystals for elimination of spurious effects, and doped single crystals for investigation of certain impurity phenomena. We report here on some methods of crystal growth of Ti_2O_3, as well as preliminary electrical measurements; the electrical characteristics of this material will be described in detail at a later date.

Because of its high melting point, which has been variously reported as 1820[1] or 1920°C,[2] high-temperature growth techniques are required to produce single crystals of Ti_2O_3. Small crystals of this material have previously been commercially grown, using an arc-type Verneuil process.[3]

II. PREPARATION OF MATERIALS

In the early stages of this work the oxide was prepared by arc melting pressed pellets prepared from titanium power and TiO_2 powder. The main impurities (in atomic parts per million relative to Ti) in crystals grown from this material were: N, 2000; Ca, 150; Al, 1500; Fe, 200.

In order to achieve higher purity, iodide titanium (Alpha Industries) was used, but it was necessary first to convert this material into a hydride in order to obtain powders suitable for mixing with TiO_2. The titanium metal was evacuated at successively higher temperatures up to 800°C in a quartz tube lined with previously outgassed Ti foil. Hydrogen, purified by passage through

palladium, was then admitted at successively lower temperatures until no further uptake occurred at 200°C. Titanium dioxide (Johnson Mathey) was fired in oxygen at 1000°C to remove water vapor and carbon. The hydride and oxide were then intimately mixed and heated at 1000°C under vacuum for sixteen hours, and the resulting powder was pressed into pellets for loading the crucible. Toward the end of this investigation, high purity Ti powder produced by the hydride process became available (Gallard and Schlesinger); this was mixed with TiO_2 and reacted in the crucible prior to growth, with satisfactory results.

III. ANALYSIS

Close control of stoichiometry is a very important factor in Ti_2O_3 growth. In early tests, oxides of various compositions were arc melted and subjected to metallographic examination. It was found that deviations of 0.03 from the nominal composition $TiO_{1.50}$ caused the material to freeze as a fine grained polycrystalline mass, whereas near the composition x = 1.50, large crystal grains formed even on quick freezing.

The stoichiometry was measured by combustion of a sample in air for sixteen hours at 1000°C to a light colored powder, and calculating the oxygen/titanium ratio (x) from the weight gain, assuming that the oxidized product was exactly TiO_2. (It was not possible by wet chemical techniques to verify whether the final product was precisely TiO_2.) A one gram sample weighed to an accuracy of 0.2 mg yields a value of x precise and reproducible to ±0.002. The twenty-two single crystals grown in this study varied in composition in the range $1.501 \leqslant x \leqslant 1.512$.

Trace impurities above the level of a few parts per million were determined in the crystals, in the crucible charge, in the starting powders, and in raw materials by mass spectrographic analysis. Nitrogen was determined by vacuum fusion and the carbon content measured by combustion of the sample and monitoring the liberated CO_2.

IV. CRYSTAL GROWTH

Crystals were grown in a tantalum resistance-heated furnace described elsewhere.[4] The melt was contained in drawn molybdenum crucibles 3.7 cm in diameter and 7 cm high; the crystals contained less than 20 ppm of Mo. (It was interesting that TiO could not be contained in Mo crucibles without severe contamination.) The furnace and crucible were maintained in a flow of titanium-gettered argon. A water-cooled molybdenum stud was used to initiate growth; in all cases a single crystal cross section was reached after less than 2 cm of growth. Crystals were usually pulled at a rate of approximately 1 cm/hr, except that heavily doped crystals were pulled at 0.5 cm/hr.

When growth was completed, the crystal was removed from the melt, the crucible temperature reduced slightly so that a solid skin formed on the melt, and the crystal was lowered to touch this surface. The electric power was then automatically diminished at a rate such that room temperature was reached overnight. One of the twenty-two crystals grown in this manner is shown in Fig. 1.

Fig. 1. Photograph of single crystal Ti_2O_3 boule 115 grown as described in the text.

The coefficients of expansion of Ti_2O_3 display an interesting anomaly in the temperature range between 0 and 350°C. On cooling through this range,

the hexagonal lattice constant a increase from 5.125 to 5.149 Å, while the hexagonal lattice constant c shrinks from 13.86 to 13.67 Å.[5] This produces a stress at any grain boundaries, so that a polycrystalline boule or melt crumbles into its single-crystal constituents on cooling. It is thus possible to separate quite large crystals from the frozen melt after crystal growth or from the arc melted buttons mentioned earlier; also this provides a visual indication of incorrect stoichiometry in the interior of the sample. The fact that the large boules remained intact on cooling is another indication that they are single crystals; these could generally be cut into oriented samples without cracking.

V. CRYSTAL STOICHIOMETRY AND IMPURITY SEGREGATION

The stoichiometry, x_c, of crystals grown in the manner described above depends on the stoichiometry of the melt, x_m, according to the empirical relation

$$x_c = 1.505 + 0.108\,(x_m - 1.505) = 1.392 + 0.108\,x_m \quad ,$$

showing that $x_c = 1.505$ when $x_m = 1.505$. The greatest deviation from ideal stoichiometry encountered so far was $x_c = 1.512$ for crystal 7-16, corresponding to $x_m = 1.57$. Attempts to obtain single crystal material with $x_c < 1.5$ have not yet met with success; according to Nishimura and Kimura[6] it is difficult to accommodate excess Ti in the corundum lattice. It was observed that for x_c close to 1.50, the interface was convex with respect to the melt; deviations from this stoichiometry led to the interface becoming concave.

In Table 1 are shown the stoichiometry and the impurities encountered in crystal 123, along with the effective distribution coefficient, $k_{eff} = c_c/c_m$ where c_c and c_m are the impurity concentrations in the crystal and melt. These results are typical of those obtained with the purer specimens. As is generally observed, most of the impurities are rejected from the crystal during growth.

Other crystals were purposely doped with much higher concentrations of V, Cr, Sc, and Fe. Table 2 lists the doping concentration and the concentration found in the grown crystal for several doped specimens. The melt was not analyzed after growth; hence, the possibility exists that evaporation from

TABLE 1

STOICHIOMETRY AND IMPURITY CONCENTRATIONS IN Ti_2O_3 CRYSTAL 123 AND IN THE MELT FROM WHICH IT WAS GROWN

Element	Concentration in Crystal – at. ppm	Concentration in Melt – at. ppm	Effective Distribution Coef.
Oxygen – x	1.507	1.526	0.27
Al	5	30	0.17
Si	20	100	–
P	1	130	–
K	1	6	0.17
Ca	1	200	0.005
V	1	1	1
Cr	24	180	0.13
Mn	3	12	0.25
Fe	27	400	0.07
Co	3	6	0.5
Ni	2	750	0.003
As	1	10	0.1
Zr	8	100	0.08
Mo	12	42	0.29
Hf	43	650	0.07
C	40	40	1
N	200*	1440*	–

*Analysis may be high due to possible contamination of the surface.

All elements determined except Na, Mg, Cu and Hg. All other missing elements below 1 ppm.

the melt could have occurred. The values cited in Tables 1 and 2 should be considered as having only semiquantitative significance.

TABLE 2
SEGREGATION IN HEAVILY DOPED CRYSTALS

Crystal No.	Dopant	Initial Conc. (at. %) in Melt	Conc. – (at. %) in Crystal
3-59	V	2.0	3.8
3-79	V	2.0	2.6
133	V	2.0	2.6
3-74	Sc	0.10	0.19
3-17	Cr	2.0	1.3

VI. ELECTRICAL PROPERTIES

The need to eliminate the N and C impurities from the samples is dramatically illustrated by electrical measurements. In the early samples, where the combined C and N content exceeded 0.8 atomic percent, the sample resistivity was isotropic, of the order of 0.025 ohm-cm, and nearly independent of temperature. This should be contrasted with the situation encountered in later samples, such as 123 (Table 1), with comparable stoichiometry and similar cationic impurity content, but whose total C and N content was below 180 ppm. For these samples the resistivity at 4.2°K was approximately 20 ohm-cm and fell to 0.052 ohm-cm at 77°K. Sample 128 which was at least as pure as sample 123, but also very close to ideal stoichiometry, exhibited resistivities for current flow parallel to the c-axis of 180,000 and 0.031 ohm-cm at 4.2 and 77°K, respectively. Purer samples also exhibited a marked degree of anisotropy, the resistivity being greatest along the c-axis.

A similar effect was encountered in magnetoresistance measurements made at 4.2°K. Boules containing C and N in excess of 0.5 atomic percent exhibited ratios of $\Delta\rho/\rho_o$ that saturated at 15 percent in magnetic fields of the order of 170 kG. For purest samples grown so far, $\Delta\rho/\rho_o$ increased with magnetic field as H^2 and exceeded a value of 3 at fields above 200 kG.

ACKNOWLEDGMENT

The authors would like to express their thanks to E. B. Owens for the analytical data and to J. T. Roddy and J. E. Eaton for material preparation and analysis in the early stages of this investigation. They are also greatly indebted to the National Magnet Laboratory for use of the high magnetic field facilities in the measurements of magnetoresistance.

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DOCUMENT CONTROL DATA – R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY *(Corporate author)*	2a. REPORT SECURITY CLASSIFICATION
Lincoln Laboratory, M.I.T.	Unclassified
	2b. GROUP: None

3. REPORT TITLE

Growth of Single Ti_2O_3 Crystals from the Melt

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Technical Note

5. AUTHOR(S) *(Last name, first name, initial)*

Reed, Thomas B. Fahey, Robert E. Honig, Jurgen M.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
11 August 1967	12	6

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
AF 19(628)-5167	Technical Note 1967-38
b. PROJECT NO. 649L	
c.	9b. OTHER REPORT NO(S) *(Any other numbers that may be assigned this report)*
d.	ESD-TR-67-343

10. AVAILABILITY/LIMITATION NOTICES

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11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
None	Air Force Systems Command, USAF

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14. KEY WORDS

titanium sesquioxide
crystal growth
anisotropy
stoichiometry